Project: eEthylen
FKZ 033RC004A
CO₂Plus Status Conference

Förderinitiative des Bundesministeriums für Bildung und Forschung
eEthylen: The Vision

Substitution of a Steam-Cracker by a CO₂-to-Ethylene Electrolyser

- Three PEM-Electrolyzer skids (SILYZER 200)
- 1.25 MW rated power (225 Nm³/h) / 2.1 MW peak power
- Highly dynamic: load changes in seconds, wide power range
- 35 bar outlet pressure
eEthylene: The Technology

• **Single step electrochemical reduction** of CO₂ in aqueous electrolytes
• The product distribution is strongly dependent on the **electro catalyst**
• **Cu based catalyst produce hydrocarbons**, Ag produce CO
• Ethylene formation involves 2 CO₂ molecules, 12 electrons, 8 water molecules to produce 1 ethylene molecule associated with 12 hydroxide ions (see picture).

Targets of eEthylene

• Find & develop a stable catalyst
• Elaborate the reduction mechanism
• Prepare a gas diffusion electrode out of the catalyst to bring the topic to industrial relevance (current density >> 200 mA/cm²)
• Scaling to x00 cm² of electrode area

eEthylene: Why ethylene – Economics
Can renewable feedstock production become economical viable?

Ratio between the **Economical Value** and the **Heating Value** for a given point in time

**Burning Processes**

<table>
<thead>
<tr>
<th></th>
<th>Energy Demand</th>
<th>Min. Energy Cost (^1)</th>
<th>Product Value</th>
<th>Cost Covering min. System Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>15,4 MWh/t</td>
<td>€463 - €694</td>
<td>€150</td>
<td>308 - 463</td>
</tr>
<tr>
<td>Ethylene</td>
<td>13,9 MWh/t</td>
<td>€419 - €629</td>
<td>€1000</td>
<td>42 - 63</td>
</tr>
</tbody>
</table>

\(^1\) electricity cost 30 €/MWh; tax & net use 15 €/MWh (there is no excess energy)

**Synthesis by Single Step Electrochemical CO\(_2\) Reduction**

<table>
<thead>
<tr>
<th></th>
<th>Energy Demand</th>
<th>Min. Energy Cost (^1)</th>
<th>Product Value</th>
<th>Cost Covering min. System Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>15,4 MWh/t</td>
<td>€463 - €694</td>
<td>€150</td>
<td>308 - 463</td>
</tr>
<tr>
<td>Ethylene</td>
<td>13,9 MWh/t</td>
<td>€419 - €629</td>
<td>€1000</td>
<td>42 - 63</td>
</tr>
</tbody>
</table>

A factor of ~4 might be enough to compensate for all losses

Thermodynamic considerations with 100% efficiency assumption
Collaboration and Workflow

Catalyst preparation:
- Preparation of powder based catalysts
- Upscaling potential
- LCA

GDE Preparation:
- Preparation of GDEs
- Evaluation of different process parameter
- Electrochemical characterization at high current densities
- Identification of intermediates/ co-products
- LCA

Characterization/ mechanistics:
- Characterization of alloys (CVD/PVD)
- In-situ deposited copper catalyst
- pre-charaterization of powder catalysts
- In-situ and operando characterization
- mechanics

Material exchange:
- information exchange
Ethylene: How we got startet?
GDE with *in-situ* grown Copper-NP catalyst in a flow cell setup

![Faradic Efficiency over time](image)

**Results**

- The maximum FE for ethylene (45 - 57%) is reached after ~50 min
- Current density of 170 mA/cm² was achieved for ethylene
- System efficiency (SE=20% @ 10 mm cathode – anode distance) (electrical energy to chemical energy)
- The full knowledge including deposition of catalyst, experimental setup and the operating condition transferred to the partners
• Dendritic structure is maintained upon oxygen Plasma treatments
• Dendrites remain stable during electrochemistry even at high potentials (U = -1.3V vs. RHE)
• Longer time treated samples preferentially form CuO agglomerates at the dendrite sharp ends
• Electrochemical reduction of CuO to Cu lead to the recovery of sharper dendrite structures
• Significant increase in the dendrite roughness after CO₂ electroreduction for the 5 min pre-oxidized samples
- Increased selectivity towards C₂ and C₃ products with increasing O₂-plasma treatment time (up to 5 minutes), especially ethanol and ethylene.
- Increased selectivity towards CO at low potentials due to roughening of the Ag substrate.
- Suppression of undesired C1 products (methane) upon plasma pre-oxidation.
XPS Analysis

- XPS measurements performed in a UHV system attached to an electrochemical cell without air exposure of the samples.
- No oxides present on the sample surface after CO$_2$RR.

EXAFS Analysis

- Absence of the oxides in the bulk of the sample during the reaction at -1.1 V for 1.5 h (red curve).
- Cu-Cu coordination numbers (CN) start low (CN = 6-7) due to initial sample oxidation but converge towards 12 (bulk Cu) after CO$_2$RR.

Large increases in the Cu-Cu CN by O$_2$-Plasma increases the catalysts performance towards the desired products.

Improved behavior is rather linked to the morphological structure than the oxidation state.
CO₂RR testing Setup
Experimental setup completed, with flow cell, gas & liquid analytics

Flow-Cell -> Catholyte

Autosampler -> HPLC

exhaust

online GC

liquid GC

Anolyte

flow : anolyte-flow
flow : catholyte-flow
flow : CO2-flow
Catalytic Testing (ABMC3 from Evonik - first sample with C\textsubscript{2}H\textsubscript{4} yield) (results reproducible within the consortium)

Testing procedure:

A) **Selectivity-Screening**

1. 2h - 50 mA/cm\textsuperscript{2}
2. 2h - 100 mA/cm\textsuperscript{2}
3. 2h - 200 mA/cm\textsuperscript{2}
4. 2h - 300 mA/cm\textsuperscript{2}

2. repetition of 1.

B) **Stability-test**

4h – 250 mA/cm\textsuperscript{2}

PEIS

4x Repetition
Catalyst Deposition:
Growth of mixed-metal samples in a PVD process (cosputtering)

Images of a homogeneous mixed-metal thin-film wafer produced by cosputtering in a PVD process as used for electrochemical characterization:

a) photograph,

b) XRF phase composition

c) XRF atomic composition Cu:Ir 70:30 (variation in overall composition: ~0.2%, the sample is overall homogeneous within this variation)
Pure Cu:
Electrochemical gaseous product formation in CO₂ saturated 0.1 M KHCO₃

Chronoamperometric step measurements
- Ethylene gas formation observed at potentials as low as -1.6 V vs. Ag/AgCl
- Voltage very similar to in-situ grown catalyst with high current density (170 mA/cm²)

Cyclic voltammetry
- Proves the observed trend
Cu-Ir (70:30 alloy): Electrochemical gaseous product formation in CO$_2$ saturated 0.1 M KHCO$_3$

**Chronoamperometric step measurements**
- Hydrogen gas evolution detected at potentials of -0.7 V vs Ag/AgCl
- No hydrocarbon (methane, ethylene) gas formation observed even at lower potentials
- Hydrogen formation is dominant over all other investigated catalytic pathways for Cu:Ir 70:30

**Result**
- The addition of iridium is detrimental for the reaction under the observed conditions, because the onset for hydrogen evolution reaction (HER) is more positive than for pure copper
Strategies of catalyst preparation

Cu-Coated Raney-Ni-Catalyst

- Raney-Ni-Powder
  - Copper coated
- Preparation of GDL
- GDL in Cu-Bath

Mixed Metal Oxide - Catalyst (MMO)

- Cu/CuO/C Catalyst
  - Drying furnace
- Cu/CuO/C Catalyst
  - Spraydryer

Phases in the spray drying of a catalyst suspension

Cu-based Catalyst

- Milled Cu-Powder
- Electrolytic Cu-Powder with dendritic surface
- Copper Foam
Upscaling of MMO-Catalyst Production

Ofeneingang:
Installation von Einhausung mit Absaugung zur
Befüllung von Kalzinationsschalen

Ofenausgang:
Installation von Einhausung mit Absaugung zum
Entleeren von Kalzinationsschalen.
Absaugung erfolgt über Absaugeinrichtung mit
Abscheidung direkt in Transportgefäss

Kalzinationsschale:
Kalzinationsschale wird mit Katalysatorpulver gefüllt;
Schütthöhe wird mit Rackel reguliert;
Kalzinationsschale mit permeabler Abdeckung

Planung Ende 2017
Umsetzung Anfang 2018
Erste Versuche in Q2/2018
Key component:
Gas Diffusion Electrode (GDE) to overcome the low solubility of CO\(_2\) in water

- Only CO\(_2\) can be electrochemically reduced not HCO\(_3^-\) or other chemically dissolved species
- 3-Phase interface ensures high CO\(_2\) concentration at the electrode (gas-liquid-solid)
  → Key challenge to achieve industrial relevant current densities
  >> 100 mA/cm\(^2\)
- CO\(_2\) is absorbed on the electro catalytic electrode
- Gas separation may be needed in subsequent processes
GDE production
Scale-up to 300cm² (MMO / Copper oxide based GDEs)

Vacuum table/ mounting
Calandaring in full with 130mm
Activation 200mA/cm²

Pore size distribution

Results

GDE with very high porosity was prepared
- Sharp pore size distribution was achieved
- 250 mbar wetting pressure
- 100 mbar bubble point pressure
- 3 Ohm resistance
- Machine sieving
  - Better homogeneity of powder layer
  - Faster application
- Calandaring
  - Homogeneous pressure over the complete roll with
Influence of copper oxide species
Characterization of Copper/ Copper-(I)-Oxides

Results

- The presence of Cu beside Cu$_2$O could slightly increase the faradaic efficiency
- All catalysts form CO, beside hydrogen and ethylene

Stability of Cu$_2$O is limited to a very small process window!

- Cu$_2$O phase is stable between pH=6 to pH=14
- The local pH value in the laminar boundary much more basic than the bulk electrolyte
- Formation of Cu$^{2+}$ azurite, malachite, tenorid, must be avoided
Comparison of Pure Copper and Pure Copper-(I)-oxide

C\textsubscript{2}H\textsubscript{4}-FE over WE-Potential

Current density over WE-Potential

Results

- Cu and Cu\textsubscript{2}O showed comparable results in the reduction experiment
## Catalyst Exchange History

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>Evonik Catalyst</th>
<th>test date</th>
<th>FE(Ethylene) @ 250mA/cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>AMC170050</td>
<td>16.02.2017</td>
<td>10</td>
</tr>
<tr>
<td>2</td>
<td>AMC170009</td>
<td>16.02.2017</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>AMC170012</td>
<td>16.02.2017</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>AMC170013</td>
<td>16.02.2017</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>AMC170014</td>
<td>16.02.2017</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>CPC SP 1700</td>
<td>16.02.2017</td>
<td>0</td>
</tr>
<tr>
<td>7</td>
<td>MC 315</td>
<td>21.02.2017</td>
<td>0</td>
</tr>
<tr>
<td>8</td>
<td>Kupferschaum</td>
<td>21.02.2017</td>
<td>4</td>
</tr>
<tr>
<td>9</td>
<td>Cu-Polyurethangewebe</td>
<td>21.02.2017</td>
<td>7</td>
</tr>
<tr>
<td>10</td>
<td>CSAZ00639</td>
<td>24.04.2017</td>
<td>2</td>
</tr>
<tr>
<td>11</td>
<td>CSAZ00640</td>
<td>24.04.2017</td>
<td>14</td>
</tr>
<tr>
<td>12</td>
<td>AMC170047</td>
<td>25.04.2017</td>
<td>0</td>
</tr>
<tr>
<td>13</td>
<td>AMC170048</td>
<td>25.04.2017</td>
<td>0</td>
</tr>
<tr>
<td>14</td>
<td>AMC170073</td>
<td>07.06.2017</td>
<td>0</td>
</tr>
<tr>
<td>15</td>
<td>AMC170050</td>
<td>07.06.2017</td>
<td>0</td>
</tr>
<tr>
<td>16</td>
<td>AMC170056</td>
<td>07.06.2017</td>
<td>0</td>
</tr>
<tr>
<td>17</td>
<td>ABMC3</td>
<td>07.06.2017</td>
<td>12</td>
</tr>
<tr>
<td>18</td>
<td>CSAZ00660</td>
<td>08.06.2017</td>
<td>12</td>
</tr>
<tr>
<td>19</td>
<td>CSAZ00661</td>
<td>12.06.2017</td>
<td>13</td>
</tr>
<tr>
<td>20</td>
<td>CSAZ00662</td>
<td>12.06.2017</td>
<td>3</td>
</tr>
<tr>
<td>21</td>
<td>CSAZ00684</td>
<td>23.08.2017</td>
<td>22</td>
</tr>
<tr>
<td>22</td>
<td>CSAZ00715</td>
<td>21.11.2017</td>
<td>25</td>
</tr>
<tr>
<td>23</td>
<td>CSAZ00716</td>
<td>21.11.2017</td>
<td>22</td>
</tr>
<tr>
<td>24</td>
<td>CSAZ00717</td>
<td>21.11.2017</td>
<td>15</td>
</tr>
<tr>
<td>25</td>
<td>CSAZ00718</td>
<td>30.11.2017</td>
<td>0</td>
</tr>
<tr>
<td>26</td>
<td>CSA200734</td>
<td>14.03.2018</td>
<td>12</td>
</tr>
<tr>
<td>27</td>
<td>CSA200733</td>
<td>14.03.2018</td>
<td>7</td>
</tr>
</tbody>
</table>

**Exchanged Samples**

- 27 different catalyst powder received from Evonik
- 120 Gasdiffusion electrodes prepared
- 37 electrodes pre-tested on 3cm² scale
- 10 electrodes tested on 10cm² scale in flow cell (longtime)
- 5 electrodes prepared on 300cm² scale (copper based)

**Highlights**

- Two suitable catalyst powders identified (mixed metal oxide)
- 25% Faraday efficiency for ethylene at 250mA/cm² achieved
- GDE preparation up scaled to 300cm²

  GDE could handle current densities J>300mA/cm²

  High mechanical stability, high porosity
Conclusion  Project eEthylene  FKZ 033RC004A

• Ethylene could be reproducibly obtained at high current densities by all partners with an in-situ deposited nano dentride copper catalyst

• Catalyst stability is still the major challenge of the whole project (we may move to other oxides)

• Electro catalysts differ significantly from classical thermochemicals catalyst with respect to composition, purity & morphology

• Copper oxide gives excellent ethylene selectivity, but could be hardly stabilized under electrochemical reduction conditions

• Transfer to gas diffusion electrodes and their implementation successful

Thanks also to the team of eEthyene
Prof. Dr. B.Roldan, F. Scholten, Prof. P. Strasser, T. Möller, Prof. K. Mayrhofer, I. Katsounaros, R. Poss, C. Reller, S. Romero-Cuellar, A. Maltenberger, D. Taroata and all the invisible technicians in the back

Thanks  Dr. Stefanie Roth for coordination